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CALPHAD aqueous solution model based on the BET approach: General theory

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Abstract

The Brunauer–Emmett–Teller (BET) model for adsorption has found extensive use in modelling of adsorption, surfaces and concentrated solutions. We present here a Gibbs energy minimiser based application of a BET and related GAB model, implemented using the ChemApp program library via ChemSheet. The basic model is constructed using solely ideal mixture phases. The use of a free energy minimizer readily enables various extensions, such as multicomponent adsorption and interactions between lattice sites. While the method presented is applicable to BET model problems in general, the emphasis in this work is on applications related to concentrated aqueous solutions.

Keywords

BET model; GAB isotherm; concentrated electrolyte solutions; adsorption; free energy minimization

Introduction

Most approaches to explaining the activity data of aqueous electrolytes include the extension of dilute solution models to moderate concentrations of the solute species. However, in highly concentrated solutions these extensions of the dilute solution models tend to be quite unsuccessful. Thus, it remains still a challenge to develop models for very concentrated solutions that would be further applicable in conjunction with an appropriate dilute solution model. The lack of both adequate property data and models for concentrated aqueous solutions hampers both the design of primary extraction processes for many metals and minerals, as well as the development of hydrometallurgical recycling technologies. In this

context the Brunauer–Emmett–Teller (BET), and related models applicable to highly concentrated solutions, could be used to shed light on the general problem.

The BET model [1] was originally presented for the adsorption of gases on solids surfaces. Later Stokes and Robinson [2] proposed the use of the BET adsorption isotherm for representing the water activities of very concentrated salt solutions, and demonstrated its application to a series of pure electrolyte solutions. Since its introduction, the aqueous BET equation has been extended to common-ion mixtures with a number of proposed mixing rules [3–5], and expressions for salt activities have been determined [6–8]. By using a different assumption regarding the adsorbtion energy, the related Guggenheim – Anderson – De Boer (GAB) equations can be derived and have also been applied to salt solutions, already first by Stokes and Robinson [2]

The method of using immaterial surface sites as additional components in Gibbs energy minimisation, originally developed by Pajarre et al. [9] as one of the key applications of the Constrained Gibbs Free energy (CFE) method, makes it possible to apply the Gibbsian method to various surface systems. Since its development, the CFE method has been applied to various systems including surface and interfacial tensions of alloys [10,11], phase diagrams of surface and nanoparticle systems [12], as well as properties of steels and melts [13,14]. The technique of immaterial surface sites is, however, quite generic and can be applied to include adsorption sites in Gibbsian calculations in arbitrary well-defined systems. With the prospect of achieving a consistent model for highly concentrated aqueous systems applicable in computational thermodynamics, it is of interest to apply the CFE technique for the properties of concentrated aqueous solutions by implementing the BET adsorption theory to the Gibbs energy minimisation calculation.

The example models, presented in the following, have been implemented using the ChemSheet program [15], which applies the ChemApp program library [16] for the thermochemical equilibrium calculations.

Theory

The Brunauer–Emmett–Teller (BET) approach is based on the Langmuir model of surface equilibria, with the assumption that the first layer of molecules adsorbing to the surface has a constant energy of adsorption and that there are no interactions between the adsorbing molecules. When applied to gaseous species, the adsorption energy of the subsequent layers after the first one is assumed to be equal to the heat of liquefaction of the adsorbing gas.

A practical equation that enables a linear plot based on experimental data to fit the model parameters was derived by Brunauer et al. [1] as

$$\frac{p}{v(p_0 - p)} = \frac{1}{v_m c} + \frac{c-1}{v_m c}\frac{p}{p_0} \quad (1)$$

where v is the total volume of the adsorbed gas, v_m the volume of the adsorbed gas in a unimolecular layer covering the surface, p is the pressure, p_0 the saturation pressure and c is a constant that approximately equals

$$c = \exp((E_1 - E_l)/RT) \quad (2)$$

where E_1 is the heat of adsorption of the gas on the surface for the first monolayer and E_l is the heat of liquefaction of the gas. Later Stokes and Robinson [2] applied the model for concentrated aqueous solutions of salts. For their formulation they made the substitutions

$$\frac{p}{p_0} = a_w \quad (3)$$

and

$$\frac{v_m}{v} = m \cdot r/55.51\frac{mol}{kg} \quad (4)$$

where a_w, is the activity of the adsorbing water, m the molality of the salt solution and r the number of adsorption sites per salt molecule, resulting in equation (5)

$$m = \frac{55.51\frac{mol}{kg} \cdot (1 - a_w)}{a_w}\left(\frac{1}{cr} + \frac{c-1}{cr}a_w\right) \quad (5)$$

The activities of salt and adsorbed water in a BET system were derived by Braunstein and Ally [7] as

$$a_s = \left(\frac{rn_S - n_{Ads}}{rn_S}\right)^r \quad (6)$$

for the salt and

$$a_{H_2O} = \frac{n_{H_2O} - n_{Ads}}{n_{H_2O}} \quad (7)$$

for the water, where n_S is the total molar amount of salt, n_{H_2O} the total molar amount of water, r the number of adsorption sites per salt species (generally not assumed to be an integer) and n_{Ads} the number of adsorbed water molecules. As an extension of the model corresponding to equations (6) and (7) Ally and Braunstein [8] later further presented an analogous equation for the activity of a salt i in a salt mixture as

$$a_{s_i} = \frac{n_{s_i}}{\sum_j n_{s_j}}\left(\frac{r_i n_{s_i} - n_{Ads_i}}{r_i n_i}\right)^{r_i} \quad (8)$$

In equation (8) n_{s_i} is the molar amount of salt i, r_i the number of adsorption sites per salt species i and $n_{Ads_i}$the number of water molecules adsorbed on salt i. In their paper, Stokes and Robinson [2] also described a modification of the BET equation derived by Anderson [17] (again, originally derived for

adsorption of a gas on a solid, but applied by Stokes and Robinson for salt solutions), where the adsorption energy differs from the heat of liquefaction by a constant amount d. The same model was also derived by means of statistical mechanics by Guggenheim [18], who noted that it is really a general case of the adsorption model where the original BET equation is obtained when $d = 0$. The model, most commonly called the Guggenheim – Anderson – De Boer model, leads to an equation where the a_w in (5) is replaced by Ka_w [2]

$$m = \frac{55.51\frac{mol}{kg} \cdot (1 - Ka_w)}{Ka_w}\left(\frac{1}{cr} + \frac{c-1}{cr}Ka_w\right) \quad (9)$$

where

$$K = e^{-\frac{d}{RT}} \quad (10)$$

The GAB equation, with one additional parameter, is also valid in somewhat more dilute solutions than the BET model. Stokes and Robinson [2] gave approximate maximum values for water activities of the respective applicability ranges as 0.3 for BET and 0.5 for GAB.

CALPHAD model

The original BET model with the water and salt (or gas and adsorption site) activities as described by Braunstein and Ally [7] (equations (*6*) and (*7*)) is equivalent to a model with two ideal lattices (or phases), one for free and adsorbed water molecules, and one for salt sites that are either free or with adsorbed water. The total number of lattice sites is n_{H_2O} in the water lattice and rn_S in the salt site lattice. The two lattices are non-interacting otherwise, but the number of sites with water adsorbed on salt, n_{Ads}, is the same in both. The standard state chemical potential difference between the free and occupied salt adsorption site is given by

$$\mu_{free}^{salt\ site,0} - \mu_{adsorbed}^{salt\ site,0} = RTlnc \quad (11)$$

equalling the energy of adsorption for the water (equation (2)). A stoichiometry corresponding to this is presented in Table 1.

Table 1. Structure of the aqueous-salt BET model

		salt	water	adsorbtion
salt site	free	1		
	adsorbed	1		1
water	free		1	
	adsorbed		1	-1

Alternative stoichiometry for the same system, but more suitable for calculating equilibrium solubilities is given in Table 2

Table 2. Structure of the aqueous-salt BET model with a solid salt included

		salt	water	adsorbtion
salt	free	1/r		
	adsorbed	1/r		1
water	free		1	
	adsorbed		1	-1
salt		1		

Here, the component 'salt' refers to the salt compound and not to an adsorption site on it, the stoichiometric coefficients related both to the free sites and those with adsorbed water are now $1/r$.

For a gas adsorption system stoichiometry can correspondingly be presented as shown in Table 3.

Table 3. Structure of the gas adsorption BET model

		surface site	gas	adsorbtion
surface	free	1	0	0
	adsorbed	1	0	1
gas	free	0	1	0
	adsorbed	0	1	-1

For systems with more than one salt, the two factors in equation (8) for activity (two terms in the corresponding chemical potential) can be split into two separate linked phases, one that is a mixture of the different salts in the system, and the other is a mixture of empty and filled adsorption sites. An example stoichiometry for the system $CaCl_2$-LiCl is presented in Table 4.

Table 4. Structure of a binary aqueous-salt BET model

		Li(+)	Ca(+2)	Cl(-)	H2O	LiCl-site	CaCl2-site	adsorbtion
water	free				1			
	adsorbed				1			-1
aq-salt	LiCl	1		1		r(LiCl)		
	CaCl2		1	2			r(CaCl2)	
LiCl-site	free					-1		
	adsorbed					-1		1
CaCl2-site	free						-1	
	adsorbed						-1	1
CaCl2*4H2O			1	2	4			
CaCl2*6H2O			1	2	6			
LiCl*H2O		1		1	1			
LiCl*CaCl2*5H2O		1	1	3	5			

With the stoichiometric structure described in Table 4, the dissolution of a solid salt (increase of the amount of "aq-salt" phase) can only happen with the simultaneous increase of the corresponding adsorption sites, for example

$$LiCl * H_2O \Leftrightarrow LiCl^{aq-salt} + r(LiCl) \cdot free^{LiCl-site} + free^{water} \tag{12}$$

The chemical potential of the dissolved salt is correspondingly given by

$$\begin{aligned}&\mu(LiCl) = \mu(LiCl * H_2O) - \mu_{free}^{water} = \mu_{LiCl}^{aq-salt} + r(LiCl)\mu_{free}^{LiCl-site} \\ &= \mu_{LiCl}^{aq-salt,0} + r(LiCl)\mu_{free}^{LiCl-site,0} + RTln\left(x_{LiCl}^{aq-salt} \cdot \left(x_{free}^{LiCl-site}\right)^{r(LiCl)}\right)\end{aligned} \tag{13}$$

There are extra degrees of freedom in setting the various standard state chemical potentials. The authors considered it simplest to set them as zero for all the species in the "aq-salt" phase and for the free (unadsorbed) species in the salt-site phases. The activity part in equation (8) is in agreement with equation (13).

In the discussion above, an ideal mixture description has been assumed for the mixture phases. Potentially useful modifications of the basic model are readily obtained if the mixture phases are described as something other than ideal. As an example, some authors [4,19] have proposed the modelling of mixed concentrated aqueous electrolyte solutions with the help of an added interaction term, which in the CALPHAD model can be added, as a normal regular solution interaction, to the "aq-salt" phase as described in Table 4.

Considering the system described by stoichiometry in Table 1, one can write a formal reaction equation

$$\text{free}^{\text{salt site}} + \text{free}^{\text{water}} \Leftrightarrow \text{adsorbed}^{\text{salt site}} + \text{adsorbed}^{\text{water}} \tag{14}$$

with an equilibrium expression

$$\mathrm{c} = \frac{(\mathrm{n}_{\mathrm{adsorbed}})^2}{\mathrm{n}_{\mathrm{free}}^{\mathrm{water}} \cdot \mathrm{n}_{\mathrm{free}}^{\mathrm{saltsite}}} = \frac{\left(1 - x_{free}^{water}\right)^2}{x_{free}^{water}\left(\frac{rm - n_{ads}/m_{water}}{55.51\frac{mol}{kg}}\right)} = \frac{\left(1 - x_{free}^{water}\right)^2}{x_{free}^{water}\left(\frac{rm}{55.51\frac{mol}{kg}} - \left(1 - x_{free}^{water}\right)\right)} \tag{15}$$

from which

$$\mathrm{c} \cdot x_{free}^{water}\left(\frac{rm}{\left(1 - x_{free}^{water}\right)55.51\frac{mol}{kg}} - 1\right) = 1 - x_{free}^{water} \tag{16}$$

Solving this for m gives

$$m = \frac{55.51\frac{mol}{kg} \cdot \left(1 - x_{free}^{water}\right)}{x_{free}^{water}}\left(\frac{1}{cr} + \frac{c-1}{cr}x_{free}^{water}\right) \tag{17}$$

Noting that with the applied ideal solution model for the phase '$water$' the mole fraction x_{free}^{water} equals the activity of the water, equation (17) is the same as the Stokes and Robinson version of the BET equation (5). Therefore the presented model structure can be used for an alternative derivation and proof of the activity expressions (6) and (7) for the BET model.

For the GAB model, equation (9) can be obtained from the free energy minimiser model, provided that the equilibrium state (as defined by molar amounts and fractions) is maintained, while the activity of water can be defined to not equal the molar fraction of the free water (x_{free}^{water}) but the molar fraction divided by the constant K ($a_w = x_{free}^{water}/K$). This can be applied by adjusting the standard state of the species in the '*water*' phase

$$\mu_{free}^{water,0} = \mu_{adsorbed}^{water,0} = \mu_{H_2O}^{0} - RTlnK \qquad (18)$$

where $\mu_{H_2O}^{0}$ is the regular standard state chemical potential of water. With this definition the activity of water is given by

$$a_w = exp\frac{\left(\mu_{H_2O} - \mu_{H_2O}^{0}\right)}{RT} = x_{free}^{water}/K \qquad (19)$$

As the adjustment of the standard state is made on both the free and adsorbed forms of the model water, equation (17) remains valid, but the molar fraction in it now describes the water activity multiplied by K and equation (9) follows. As the values of the constant K applied are less than unity, the adjusted standard state chemical potential is higher than the original value, making the GAB model unstable in dilute range relative to any realistic thermodynamic description of such a solution. The adjusted standard state also follows from the assumption that the adsorption energy (from gaseous to liquid state) differs from the heat of liquefaction.

Conceptually, the model presented here differs from the earlier BET and GAB models; in the new model both the water and each salt type now formally exist as two different species in their free and adsorbed forms. Total amounts of water and salt sites are the same in both, as are the chemical potentials and activities of the free forms. Also, the total free energy (for simplicity here written for a single salt and solvent) of the system is the same as in the current model, as now the Gibbs free energy is given by:

$$\begin{aligned} \mathrm{G} &= n_{free}^{water}\mu_{free}^{water} + n_{adsorbed}^{water}\mu_{adsorbed}^{water} + n_{free}^{salt}\mu_{free}^{salt} + n_{adsorbed}^{water}\mu_{adsorbed}^{water} \\ &= n^{water}\mu_{free}^{water} + n^{salt}\mu_{free}^{salt} \end{aligned} \qquad (20)$$

The chemical potential of the adsorption component in the model is not zero, but it has no contribution to the total free energy, as its total amount over all species is zero leading to equation (20). This chemical potential, π_{ads}, can be expressed based on the activities of either water or the solute salt in single salt system as

$$\frac{\pi_{ads}}{RT} = ln\frac{x_{free}^{water}}{1 - x_{free}^{water}} = \ln\left(\frac{1 - (a_{salt})^{\frac{1}{r}}}{(a_{salt})^{\frac{1}{r}}c}\right) \quad (21)$$

In equation (21) x_{free}^{water} is related to the activity of the water by equation (19) in the GAB model and is equal to it in the BET model. The activity of the salt species (a_{salt}) in the equation is based on the standard state used in the BET and GAB models. The corresponding equation in a salt mixture system is

$$\frac{\pi_{ads}}{RT} = ln\frac{x_{free}^{water}}{1 - x_{free}^{water}} = \ln\left(\frac{1 - \left(a_{salt_i}/(x_{salt_i}\gamma_i)\right)^{\frac{1}{r}}}{\left(a_{salt_i}/(x_{salt_i}\gamma_i)\right)^{\frac{1}{r}}c}\right) \quad (22)$$

where

$$x_{salt_i} = \frac{n_{salt_i}}{\sum_j n_{salt_j}} \quad (23)$$

and γ_i is the activity coefficient for the species i applied in the 'aq-salt' phase (unity in the simplest case with ideal mixtures).

Calculation examples

Example calculation results for adsorption of N_2 gas on a Fe-Al2O3 catalyst are shown in Figure 1. Experimental data points and model parameters are taken from Brunauer et al. [1]. In the paper, the amount of catalyst was given as 50.4 g and V_m as 133 cm^3 (STP) and the parameter c as 156.7. The number of adsorption sites (capable of adsorbing one molecule of N_2) for a stated amount of catalyst is given by

$$n_{surface\ site} = \frac{1atm \cdot V_m}{R \cdot 298K} \approx 0.005436\ \text{mol} \quad (24)$$

and is used as an fixed input value for the calculations. The molar amount of adsorbed gas in the system is varied and its value is plotted as a function of p/p_0 (gas activity in the model)

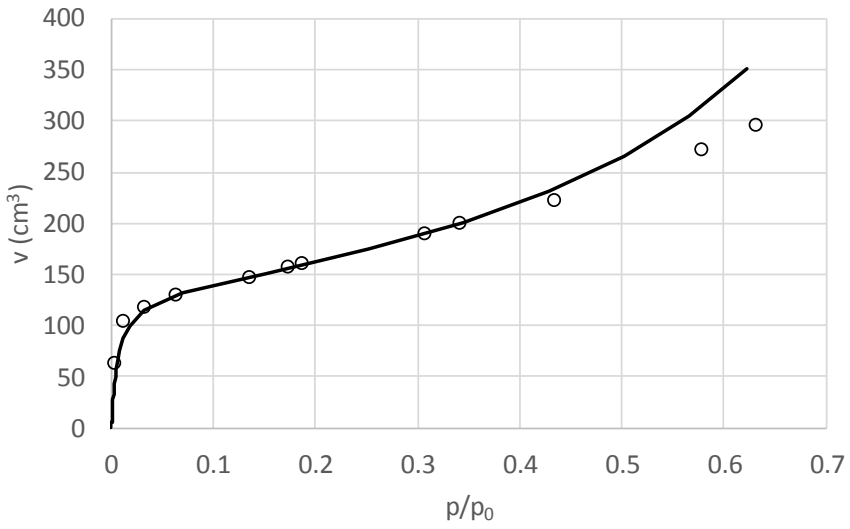

Figure 1. Adsorption of N_2 on a Fe-Al2O3 surface. Model curve compared with experimental data points.

Analogous examples for aqueous systems are illustrated in Figure 2. The parameters for NaOH and LiBr have been adopted from Stokes and Robinson [2], with *r* = 3.2 and *c* = 19.3 for NaOH and *r* = 3.82 and *c* = 43 for LiBr. The CFE model feed amounts are given as 1 kg of free water and $r \cdot m$ moles of free salt sites for a solution molality m. The experimental results for osmotic coefficient values shown are from Hamer and Wu [20].

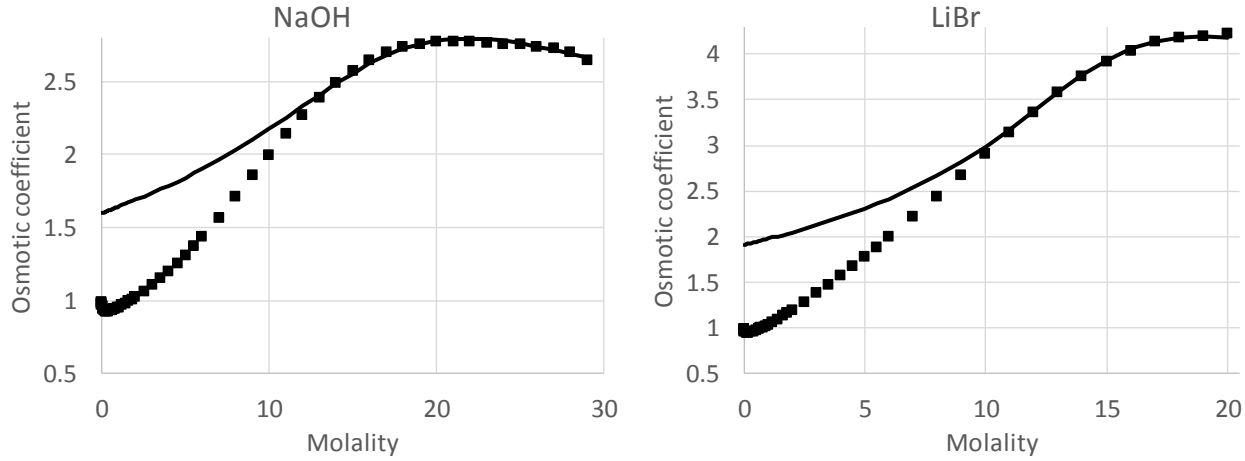

Figure 2. Osmotic coefficient in the aqueous NaOH and LiBr systems at 25 °C. BET-model curves compared with experimental data points

Calculation results for a binary salt mixture corresponding to the model structure presented in Table 4 for a $CaCl_2$-LiCl system are shown in Figure 3. The solid phases and the thermodynamic data are taken from the work of Zeng et al. [19]. Using their parameters, the solubility isotherms at 298.15 K are reproduced by the current method in Figure 3. The model applies, like in Zeng et al. [19], a regular solution like interaction between LiCl and $CaCl_2$ salts in solution. In the current method it is formally defined for the “aq-salt” phase.

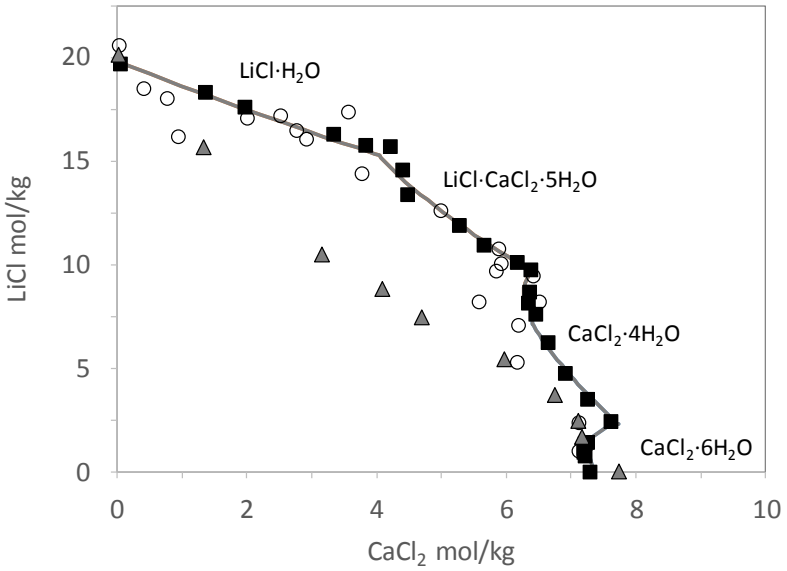

Figure 3. Solubility isotherms in aqueous CaCl2-LiCl2 system at 298.15 K. Model parameters and collected experimental data from three sources as in Zeng et al. [19].

In Figure 4, the experimental osmotic coefficient from Hamer and Wu [20] is compared to model results obtained from applying the BET model and the GAB model using the values applied by Stokes and Robinson [2], and refitted parameters to the GAB equation, when the value of parameter r was chosen for best fit. Also shown is the model curve applying the Pitzer equation with parameters from Pitzer [21], with the typical validity extending from infinite dilution up to 6-8 mol/kg systems. The complementary qualities of

the GAB and Pitzer curves in this concentration range are obvious.

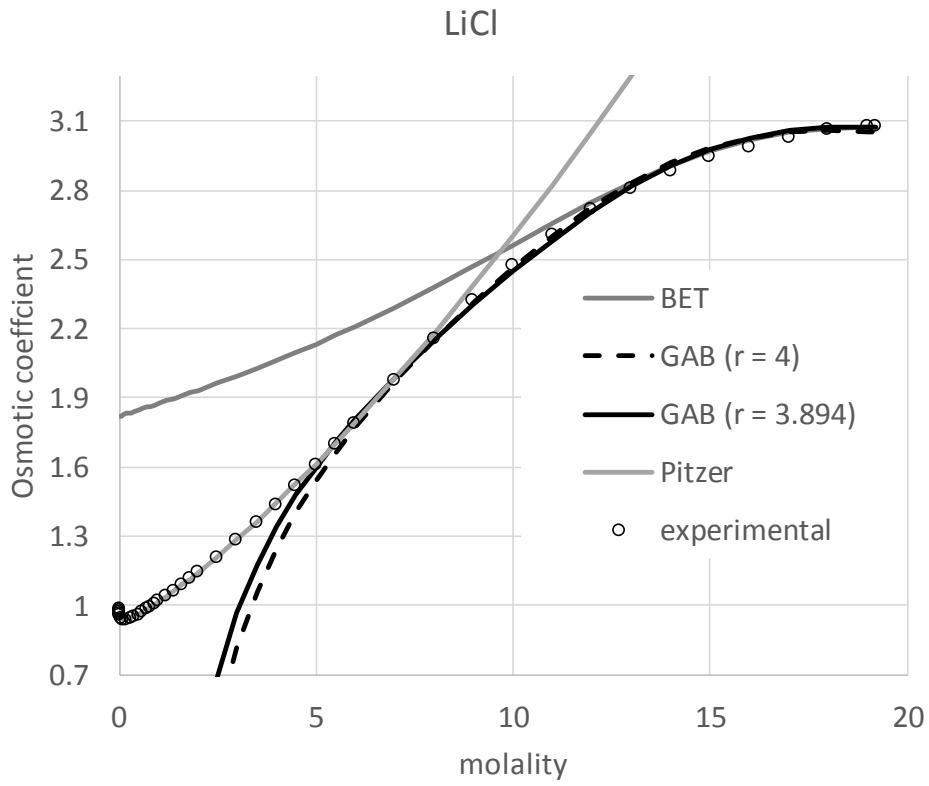

Figure 4. Experimental and modelled osmotic coefficients of LiCl. Parameters for the refitted GAB model were r = 3.894, K = 0.88 and c = 16.88.

Discussion and conclusions

The BET and GAB models for adsorption from a gas or concentrated aqueous solution have been implemented using a general free energy minimizing program. The basic model is achievable through the use of ideal mixture phases with linked stoichiometries. The possibility of using other mixture descriptions for either the adsorbing gas/water phase or the adsorbent surface/salt allows for various modifications to the basic model. One of the previously presented binary interaction systems was implemented by applying a regular solution model for the salt species.

The BET model is a simple and useful technique for calculating the ionic activities in concentrated systems as it contains only two parameters that have little temperature dependency [2,22]. The GAB model has an additional parameter, but achieves a wider validity range and has the potentially useful property of not being the stable phase (with the lowest free energy) outside its validity range. The osmotic coefficients of water were also calculated with the Pitzer and GAB models for a simple LiCl aqueous system, indicating a fair complementary quality as regards their range of validity in terms of the molality of the solution. Even

though presented with this one example, it is well known that the GAB model agrees with experiments for several systems in the high molality range, while the Pitzer model is recognised as the conventional means of modelling multicomponent aqueous solutions in dilute and moderate concentrations. A subsequent study will be focused on the respective (complementary) stability of the Gibbs energies presented with the GAB and Pitzer models in their mutual range of validity in the pursuit of a consistent technique for calculation of the aqueous solutions from the infinite dilution limit to extremely high concentrations.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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